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18 JUN 1999

18JUN99 E455378-1 C16545
P01/7700 0.00 - 9914101.2

Request for grant of a patent

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The Patent Office

Cardiff Road
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1. Your reference RS001LS/1

2. Pa
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3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

THE UNIVERSITY OF WALES, BANGOR
THE BIOCOMPOSITES CENTRE
BANGOR
GWYNEDD
LL57 2UW

Patents ADP number *(if you know it)* 7269319002

If the applicant is a corporate body, give the country/state of its incorporation

4. Title of the invention TREATMENT OF OILS

5. Name of your agent *(if you have one)* NONE 5732417002

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

SARA HUGHES
THE BIOCOMPOSITES CENTRE
UNIVERSITY OF WALES
BANGOR
GWYNEDD LL57 2UW

Patents ADP number *(if you know it)*

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Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

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a) any applicant named in part 3 is not an inventor, or
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Description	7
Claim(s)	0
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Priority documents	0
Translations of priority documents	0
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	1
Request for preliminary examination and search *(Patents Form 9/77)*	0
Request for substantive examination *(Patents Form 10/77)*	0
Any other documents *(please specify)*	0

11. I/We request the grant of a patent on the basis of this application.

Signature Paul Fowler Date 17 June 1999

12. Name and daytime telephone number of person to contact in the United Kingdom SARA HUGHES 01248 370588

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Treatment of Oils

This invention relates to curable compositions, more particularly it relates to curable compositions which, once cured, are excellent bonding agents for composites made of wood and other organic materials. It is well known to use aldehydes as components of compositions which, on polymerisation or curing, bond wood composites. Such compositions include urea formaldehyde and phenol formaldehyde resins.

The compositions of the present invention are formulated using aldehydes prepared from rape seed oil. Among the triglycerides contained by rape seed oil are those based on erucic acid. Such triglycerides contain unsaturated moieties in their structure which can be reacted with ozone in a solvent. The products of ozone treatment are either ozonides or hydroperoxides depending on the solvent used. Hydroperoxides are produced when alcohols such as methanol or ethanol are present either alone as the solvent, or in admixture with other solvents. Ozonides are produced when, for example, chlorinated solvents such as dichloromethane are used. Both ozonides and hydroperoxides when treated with a reducing agent undergo reductive cleavage and aldehydes are formed.

The compositions of the present invention are based on the use of aldehydes formed in this way from rape seed oil.

The production of so called aldehyde oils from soya bean oil has been described in Journal of the American Oil Chemists' Society (JAOCS) 38 (1961) 375-379. This article also describes small scale attempts to form resinous materials using the aldehyde oils, and it is stated at page 378 that 'the polyfunctionality of aldehyde oils is sufficient to cause crosslinking.'. It is also stated at page 379, that 'The resin forming reactions were carried out on a small scale on a purely exploratory basis.'

We have now found that aldehydes derived from the treatment of rape seed oil may be utilised in curable compositions using either an acid or alkaline catalyst.

According to the invention therefore there is provided a curable composition containing at least one aldehyde component which has been formed by a process in which rape seed oil is reacted with ozone to form products which on reductive cleavage form aldehydes.

The reductive cleavage may be carried out using catalytic reduction with hydrogen, or by the use of zinc and acetic acid. We prefer to carry out the reductive cleavage where the products of the treatment with ozone are hydroperoxides using a reducing sugar. In this case the sugar will be oxidised during its use as a reducing agent. This need not be separated from the products of the ozone treatment, so that the curable composition thereby contains an oxidised sugar, which because of its acidic nature may assist in the curing reaction. We also prefer to use an excess of sugar so that unreacted sugar is present in the product as it appears to aid in maintaining the stability of the product storage.

We have found that alpha-D-glucose can be used to perform the reductive cleavage. Other sugars that can be used include mannose, allose, galactose, and maltose.

In another form of our invention we use the rape meal, which either still has its full oil content, or from which the oil has not been fully extracted, as a starting material for the production of the aldehyde component of the curable composition. In this way we produce a curable composition which contains rape meal as an extender of the composition when used in bonding composites, or forms the matrix of a cast or moulded body. The rape meal is present because the process of reacting ozone with rape seed oil follows an additional step where rape seed oil is wholly or partially extracted from rape meal by means of a solvent, and the solvent, rape seed oil and meal mixture is then used in the aldehyde forming process so that the meal becomes a component of the curable composition. The solvent is wholly or partially removed from the rape meal aldehyde mixture before it is incorporated in the curable composition or used without addition of any other components to the composition.

We prefer to use a curable composition where an aldehyde component has been formed by a process in which the solvent present during the treatment with ozone is an alcohol, such as ethanol or methanol. The alcohol may be used in admixture with other solvents such as hexane. We have also found that industrial methylated spirit (IMS) can be used as the solvent during the treatment with ozone.

Other solvents that can be used include chloroform, dichloromethane, hexane, and cyclohexane. The ozone may be used at concentrations in the range 1 to 10 % in oxygen and is preferably contacted with the oil until ozone is no longer absorbed by the reaction mixture. The end point can be judged using Thin Layer Chromatography (TLC). This test is used to check periodically for the end point i.e when none of the components present in the starting oil are present in the reaction mixture, or when no ozone is present in exit gases. The ozone treatment may be carried out at low temperatures in the range e.g $-10°$ to $-78°$ Centigrade, but may also be carried out at ambient temperatures of the order of 25°C. Though the temperature of the reaction mixture may rise on introduction of ozone to as high as 45°C it is preferable to operate at temperatures below 25°C.

The compositions may contain curing catalysts which may be acids or alkali. We prefer to use as an acid catalyst, para toluene sulphonic acid.

We have further found that the addition of an acid, particularly a sulphonic acid such as p-toluene sulphonic acid, followed by treatment with a base, results in an aqueous system which is either very finely dispersed in water or wholly or partially water soluble. No residue can be detected when the aqueous material is filtered through Whatman No 1 filter paper and a glass wool column.

In addition to the acid or base catalyst, one or more of the following can be added as components to the curable composition: glycerol, furfural, furfuryl alcohol, phenol, cashew nut shell liquid, maleic anhydride and urea.

We have found in particular that the presence of furfuryl alcohol in a composition renders the composition curable at ambient temperatures.

We believe that the use of rape seed oil as a source of the aldehydes used in the curable compositions of the invention is particularly advantageous due to the presence of glycerides based on erucic acid. We believe that when the curable compositions are, for example, used as binders for particulate wood boards, the fact that the aldehydes are derived from glycerides based on erucic acid confers a desired hydrophobicity and flexibility on the binder. This is also important in making composites from other cellulosic plant materials such as wheat straw, hemp, jute, flax, rice straw, and maize. The waste meal from oil extraction can also be bonded satisfactorily.

The following examples illustrate but do not limit the invention.

Example 1
Preparation of Triglyceride aldehydes:

A solution of 400 g (≈0.5 mole) of Rape Seed Oil (RSO) in 2 litre dichloromethane is cooled at −78°C. The solution is stirred with a powerful overhead stirrer. Ozonised oxygen gas containing approximately 33.3 mg of ozone per litre of gas is bubbled through the solution at the rate of 10 litres/min until one molar equivalent of ozone has been absorbed (6 hours). The reaction is monitored by TLC (Silica gel plate, developed in 20:80 ether and petroleum spirit solvent systems). 1 litre of acetic acid is added, followed by the addition of 320 g of zinc while the solution is stirred vigorously. The solution is allowed to warm very slowly to room temperature. Stirring is continued for 2 more hours. Zinc is filtered off at reduced pressure. Dichloromethane is removed under reduced pressure and the oxidised product is extracted from ether/water partition. Ether is removed by evaporation to give the final product (RSO aldehyde, 398.0 g).

Example 2

A solution of 30 g (≈0.08 mole) of RSO in methanol (200 ml) is cooled at −10°C with overhead stirring. Ozone (at an unknown concentration) in oxygen is bubbled through the solution at the rate of 5.0 litres/min until no starting material can be detected by TLC (Silica gel plate, developed in 20:80 ether and petroleum spirit). Alpha-D-Glucose (5 g) is dissolved in alkaline water (pH 10) and added to the ozonation product of RSO with continued vigorous stirring. The solution is allowed to warm slowly to room temperature, heated at 60°C for 2 hours. The product is a off white paste that becomes a solution on addition of acids. The product is repeatedly extracted using a 1:1 ether/water mixture until a clear solution is observed in the aqueous phase. Removal of the ethereal phase affords RSO aldehydes.

Example 3

30 g of rape seed oil is dissolved in 200 ml of IMS and placed in a reaction vessel with overhead stirring. Ozone in oxygen is bubbled through the solution at a rate of 10 litres per minute until no starting material can be detected by TLC. 14 g of alpha-D-Glucose is dissolved in 50 ml of water and added to the reaction mixture. The mixture is heated to 50° C for 2 hours and allowed to cool and left at 25° C overnight. The solvent is removed under reduced pressure. The RSO aldehydes separate as an oily layer from the water on standing. The oily layer contains oxidised and unreacted sugar.

Example 4
Test of bond strength

Acid catalysed compositions were made up to the formulations shown in Table 1 and the bond formed by the cured composition was tested.

The bond strength for acid catalysed composition is measured by specially designed equipment called ABES (Automated Bond Evaluation System). Specially cut and sized veneer of wood is used. Resin is smeared on the test strip on an area of 4 mm x 20 mm and pressed with two mini pre-heated platens. After certain period of time the platens are removed from the bond area, and the bond is cooled by compressed air for 20 seconds, followed by pulling in a shear mode. Pulling continues until the bond fails. The formulations were tested using a press time of 3 min at 180°C.

Table 1

Formulations		**Bond strength (mPa)**
Crude RSO aldehyde (example 3) Para-toluene sulphonic acid (hereafter p-TSA)	1.0g 0.2g	5.00
Extracted RSO aldehyde (example 2) p-TSA	1.0g 0.2g	4.04

Example 5
Preparation of acid catalysed composition from RSO aldehyde:

p-TSA (0.2g) is dissolved in 0.2 g of methanol to which 1g of RSO aldehyde is added. A thin paste is formed by stirred vigorously with a glass rod.

The formulations listed in Table 2 were tested using ABES with a press time of 3 min at 180°C. The formulations containing no curing catalyst are included to show that in order to get a satisfactory bond strength, a catalyst is needed.

Table 2 Bond strength for acid catalysed RSO resin formulations

Formulations		**Bond strength (mPa)**
RSO aldehyde alone		0.40
RSO aldehyde p-TSA (51 % in MeOH)	1.0 g 0.4 g	4.47
RSO aldehyde p-TSA (51% in water)	2.0 g 0.4 g	4.43
RSO aldehyde Glycerol	3.0 g 0.2 g	1.35
RSO aldehyde Glycerol p-TSA (51% in water)	4.0 g 0.2 g 0.4 g	4.16
RSO aldehyde Glycerol p-TSA (51% in water)	5.0 g 0.4 g 0.4 g	3.86
RSO aldehyde Ethylene glycol	6.0 g 0.2 g	1.84
RSO aldehyde Ethylene glycol p-TSA (51% in water)	7.0 g 0.2 g 0.4 g	4.08
RSO aldehyde Ethylene glycol p-TSA (51% in water)	8.0 g 0.4 g 0.4 g	5.01
RSO aldehyde Furfuryl alcohol p-TSA (51 % in MeOH)	1.0 g 0.5 g 0.4 g	5.56
RSO aldehyde Furfuryl alcohol p-TSA (51 % in water)	1.0 g 0.2 g 0.2 g	5.35
RSO aldehyde Phenol p-TSA (51 % in MeOH)	1.0 g 0.5 g 0.4 g	5.77
RSO aldehyde CNSL p-TSA (51 % in MeOH)	1.0 g 1.0 g 0.4 g	4.81
RSO aldehyde Urea p-TSA (51 % in MeOH)	1.0 g 1.0 g 0.4 g	3.36

Table 2a Effect of maleic anhydride* (hereafter MA) on acid catalysed RSO resin.

Formulati ns		Bond strength (mPa)
RSO aldehyde alone		0.40
RSO aldehyde p-TSA	1.0g 0.2 g	4.48
RSO aldehyde MA p-TSA (Solid)	0.7 g 0.3 g 0.2 g	5.31
RSO aldehyde MA p-TSA (solid) Furfuryl alcohol	0.7 g 0.3 g 0.2 g 0.2 g	5.35
RSO aldehyde MA Glycol p-TSA (solid)	0.7 g 0.3 g 0.4 g 0.2 g	5.51
RSO aldehyde MA Glycol p-TSA (solid) Furfuryl alcohol	0.7 g 0.3 g 0.4 g 0.2 g 0.2 g	5.25

* The maleic anhydride was added in molten form.

Example 6

Base catalysed compositions formulated as shown in Table 3 were tested using ABES with a press time of 3 min at 180°C.

Table 3 Base catalysed RSO composition

Formulations		Bond strength (mPa)
RSO aldehyde alone		0.40
RSO aldehyde NaOH (30 %)	1.0 g 0.4 g	1.85
RSO aldehyde NaOH (13.6 %)	1.0 g 0.4 g	1.80
RSO aldehyde Urea NaOH (30 %)	1.0 g 0.2 g 0.4 g	2.38
RSO aldehyde Urea NaOH (13.6 %)	1.0 g 0.2 g 0.4 g	2.02
RSO aldehyde Glycerol NaOH (13.6 %)	1.0 g 0.4 g 0.4 g	1.69

RSO aldehyde	1.0 g	2.43
Ethylene glycol	0.4 g	
NaOH (13.6 %)	0.4 g	

The compositions were formulated using aqueous NaOH, hence the relatively low bond strengths at the pressing times used. Higher bond strengths can be obtained by using longer press times.

Example 7

A mixture of 1000 g of ground rapemeal in 2 litres of IMS is maintained at about 20°C with overhead stirring. Stirring continued for an hour so as to extract oil into the solvent. Ozone in oxygen is then bubbled through the mixture at 10 litres/min until no soluble starting material can be detected by TLC (silica gel plate, developed in 2:80 ether and petroleum spirit). An aqueous saturated solution of alpha-D-Glucose (33g) is added to the mixture and held at 40°C for about 3 hours, when substantially all the solvent is removed under reduced pressure. The meal containing the aldehydes formed by the treatment with the sugar is dried at room temperature and then in an oven at 65°C to a moisture content of about 4%. 110g of the dried meal is mixed with 5g furfuryl alcohol and 3g para toluene sulphonic acid and pressed at 180°C for 3 minutes to form a cured body.

Example 8

1g of RSO aldehyde, prepared as described in Example 3, is mixed with 0.2g of para toluene sulphonic acid which had been dissolved in water. Furfural alcohol (0.2 g) was then added with stirring and the mixture allowed to stand. The mixture set to a solid plastic material after 4 hours. Another quantity of the mixture was prepared and cast into a film and allowed to set.

ABSTRACT

Treatment of Oils

This invention relates to a curable composition containing at least one aldehyde component which has been formed by a process in which rape seed oil is reacted with ozone to form products which on reductive cleavage form aldehydes.

PCT/GB97/02220